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The influence of multi-valent dopants in diffusion related phenomena is complex. For situations where grain boundary diffusion predominates, factors such as grain boundary segregation and compensating defects may have countervailing influences. These are highly pertinent issues when considering the efficacy of high temperature coatings, where failure of the underlying substrate is driven by oxidation. Accordingly, the influence of impurities on the rates of both inward diffusion of oxygen, and outward cation diffusion is critical.

On this note, work has initiated on simulating the distribution of a diffusing species within a medium where both rapid and slow diffusion paths exist. In practice this could be a sintered polycrystal, a thermally sprayed coating, or a fibrous composite material. Once developed, it is believed that such a model would be a valuable tool in the lifetime prediction of components, as well as the design and selection of oxidation resistant coatings.

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# Tailoring of Grain Boundary Chemistry to Produce Super Creep-Resistant Alumina

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## Objectives

Identification of new dopant systems with further enhancement to the high temperature creep properties of alumina, together with elucidation of the mechanism(s) by which the impurity ions affect the creep process.

## Status of Effort

The influence of multi-valent dopants in diffusion related phenomena is complex. For situations where grain boundary diffusion predominates, factors such as grain boundary segregation and compensating defects may have countervailing influences. These are highly pertinent issues when considering the efficacy of high temperature coatings, where failure of the underlying substrate is driven by oxidation. Accordingly, the influence of impurities on the rates of both inward diffusion of oxygen, and outward cation diffusion is critical.

On this note, work has initiated on simulating the distribution of a diffusing species within a medium where both rapid and slow diffusion paths exist. In practice this could be a sintered polycrystal, a thermally sprayed coating, or a fibrous composite material. Once developed, it is believed that such a model would be a valuable tool in the lifetime prediction of components, as well as the design and selection of oxidation resistant coatings.

## Accomplishments/New Findings

In the early stages of the program, the studies focussed on dopant ions such as Y, La, and Nd, which are isovalent with Al. More recently, the research has expanded to include dopant systems such as Fe and Ce, where the valency of the impurity ion is variable. In the case of Fe doping, the valence state is Fe(III) in air, which can be converted to Fe(II) under reducing conditions. For doping with Ce, the change in valence state of interest is from Ce(IV) under oxidizing conditions, to Ce(III) under reducing conditions. The rationale behind this work was to test the relative importance of factors such as ionic size and compensating defects in determining the creep behavior. For ease of reference, the ionic radii of selected elements are shown in Table I. In addition to tensile creep testing, densification studies were undertaken.

Such studies are of interest not only in their own right, but represent an experimentally expedient manner of probing the effect of the dopant on the diffusion kinetics.

| Element | Ionic Charge | Ionic radius (nm) |
|---|---|---|
| Aluminum | 3+ | 0.51 |
| Yttrium | 3+ | 0.89 |
| Iron | 2+ | 0.74 |
| Iron | 3+ | 0.64 |
| Cerium | 3+ | 1.03 |
| Cerium | 4+ | 0.92 |

Table I: Ionic radii of selected cations

The densification kinetics of samples doped with 1000 ppm Fe were carried out in both oxidizing and reducing conditions. In the case of the latter, a 5 % hydrogen in nitrogen mix was used to achieve an oxygen partial pressure ( $pO_2$ ) of $\sim 10^{-14}$ . A similar set of studies was performed with samples co-doped with 1000 ppm Fe and 1000 ppm Y. All heat-treatments were carried out at 1350 °C. The densification curves for the various samples are depicted in Figure 1. Note that each data point represents a single sample, and the error bars indicate the degree of experimental uncertainty in the density measurement. When considering the effect of oxygen partial pressure, it was consistently observed that the densification kinetics of Fe-doped samples sintered under highly reducing conditions were more rapid than that of Fe-doped samples sintered in air (see Figure 1 a). This relative trend is consistent with the early work done on this system by Rao and Cutler [1] and Hollenberg and Gordon [2]. However, differences arise between the various studies when comparing the behavior of the Fe(III) doped samples with that of undoped alumina. Thus whereas Hollenberg and Gordon reported that under oxidizing conditions, the addition of Fe did not alter the creep rate, our studies show that both the densification and the tensile creep rates were *slowed* by the Fe doping. Although factors such as experimental procedure and powder purity may play a role, it is believed that the reason for this discrepancy lies primarily with the different diffusion mechanisms. For the relatively coarse

grained materials studied by Hollenberg and Gordon, lattice diffusion predominates, hence the enhancement in diffusion kinetics was rationalized with respect to the compensating ionic defects. In contrast, the grain size of the samples studied at Lehigh was submicron, so that grain boundary diffusion is the primary mechanism. In this case, it is argued that diffusion dependent processes are slowed, because the presence of compensating defects is mitigated by the segregation of the Fe ions to the alumina grain boundaries.

In the case of the co-doped compositions, it is interesting that the addition of 1000 ppm Fe to 1000 ppm Y-doped alumina has a negligible influence on the densification behavior (see Figure 1b). The suggestion, therefore, is that the diffusion inhibiting effect of the Y ions (which are known to be strongly segregated to the alumina grain boundaries), predominates. Nonetheless, under reducing conditions, there is an relative enhancement in the densification rate. This is consistent with the observations on the singly Fe-doped samples, and again points to a role of compensating defects.

Cerium was selected as a dopant because of its variable valency and large ionic radius relative to the $Al^{3+}$ ion (see Table I). To the authors' knowledge, there are no previous studies which address the effect of Ce additions on the creep and densification behavior of alumina. The effect of doping with 1000 ppm Ce on the creep behavior is shown in Figure 2, where creep data derived from different dopant systems have been normalized for a grain size of 2.4 micron. It can be seen that the addition of 1000 ppm Ce is not as beneficial as Y-doping. Examination of crept specimens in the analytical electron microscope confirmed that the Ce ions were strongly segregated to the alumina grain boundaries. The valence state of the Ce ions was determined from electron energy loss spectra, and found to be Ce (IV). Preliminary densification studies carried out on Ce-doped samples have indicated that densification is enhanced under reducing conditions, where the Ce is presumably in the trivalent state. This trend is different from what was observed for the Fe doped samples, because in this case, the *isovalent* state of the dopant ion, (i.e., +3) resulted in the more rapid kinetics. More work needs to be undertaken to understand this behavior.

*References*

1. W. Raja Rao and I.B. Cutler, "Effect of Iron Oxide on the Sintering Kinetics of Alumina," J. Am. Ceram. Soc., 56 (1973) 588-93

2. G. Hollenberg and R.S. Gordon, "Effect of Oxygen Partial Pressure on the Creep of Polycrystalline Alumina Doped with Cr, Fe or Ti," J. Am. Ceram. Soc., 56 (1973) 140-7
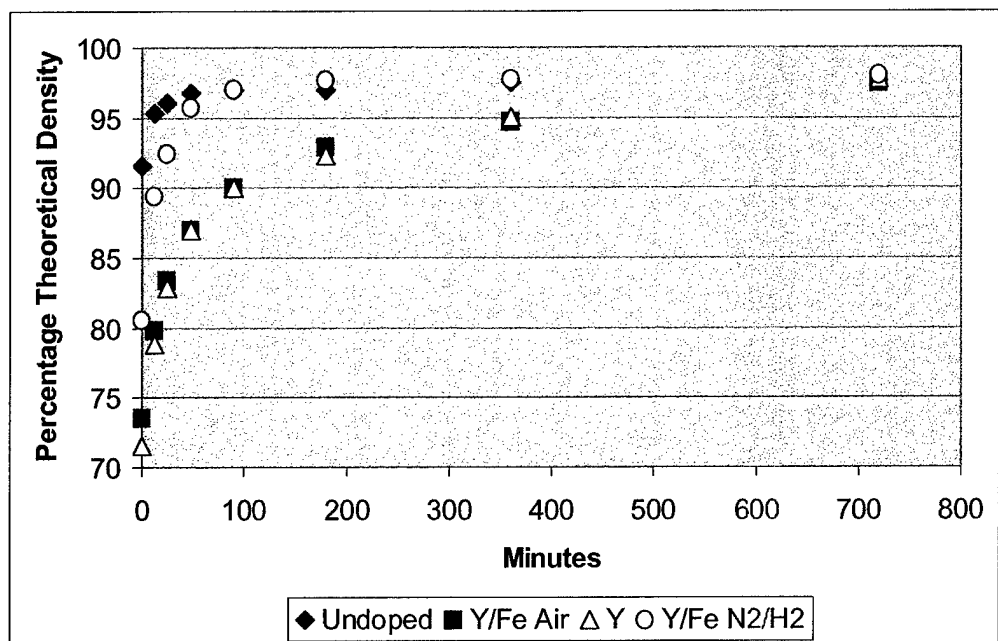
a)
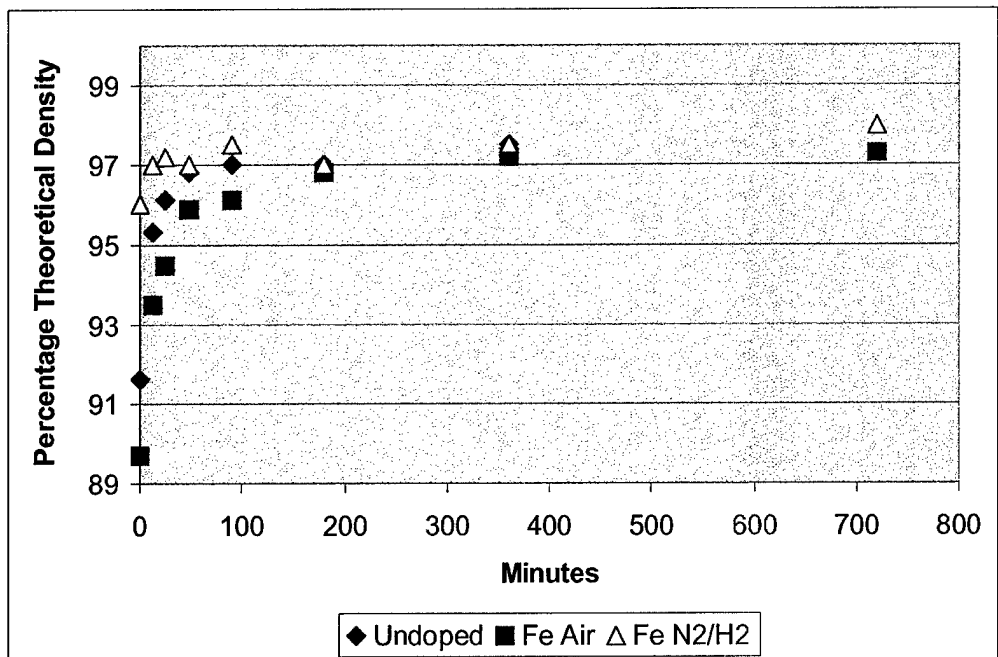


b)



Figure 1: Effect of atmosphere on alumina densification curves measured at 1350 °C: a) Singly doped samples (1000 ppm Fe) and b) co-doped samples (1000 ppm Fe/1000 ppm Y).
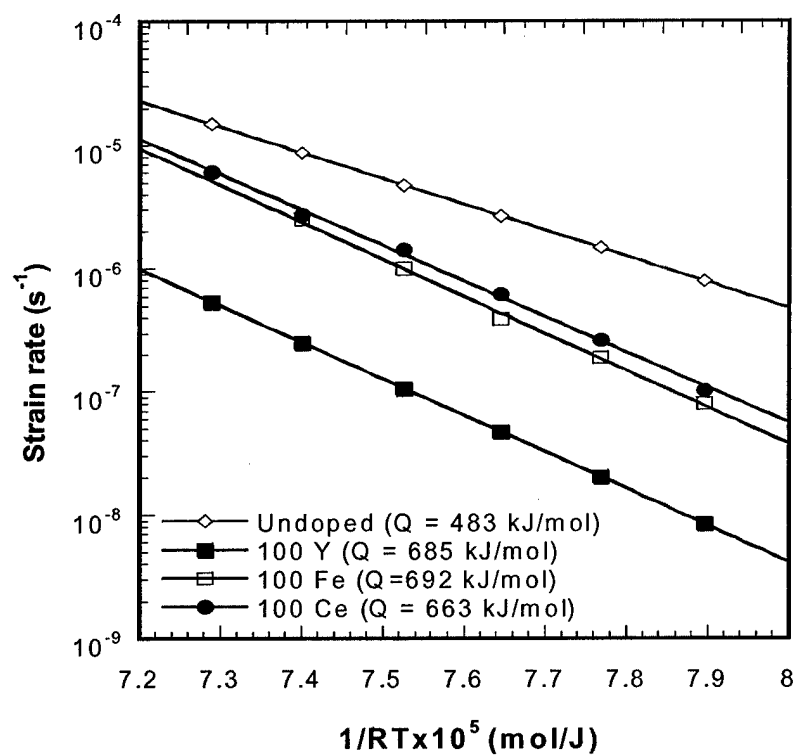
Figure 2: Comparison of creep behavior (in air) for alumina containing 100 ppm of various dopant ions (Ce, Fe, Y).

## Personnel

| | |
|---|---|
| Martin P. Harmer: | Principal Investigator |
| Helen M. Chan: | Co-Principal Investigator |
| Jeffrey M. Rickman: | Co-Principal Investigator |
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## Publications

W.S. Tong, J.M. Rickman, H.M. Chan and M.P. Harmer, "Coble-Creep Response and the Variability of Grain Boundary Properties," J. Mater. Res., J. Mater. Res., 17 (2002) 348-52

C. Wang, G.S. Cargill III, H.M. Chan and M.P. Harmer, "X-Ray Absorption Near Edge Structure of Grain Boundary Segregated Y and Zr in Creep Resistant Alumina," J. Amer. Ceram. Soc., 85 (2002) 2492-98

C.-M. Wang, H.M. Chan and Martin P. Harmer, "Effect of $Nd_2O_3$ Doping on the Densification and Abnormal Grain Growth Behavior of High Purity Alumina," J. Amer. Ceram. Soc., in press.

## Interactions/Transitions

M. Drahus, C. Turquat, H.M. Chan and M.P. Harmer, "The Effect of Iron on the Grain Boundary Segregation Behavior of Yttrium in Alumina," 105th Annual Meeting of the American Ceramic Society, Nashville, TN, April 27 - 30, 2003.

C. Turquat, M. Drahus, J.M. Rickman, H.M. Chan and M.P. Harmer, "Cerium-Doped Alumina: From Microanalysis to Creep," 105th Annual Meeting of the American Ceramic Society, Nashville, TN, April 27 - 30, 2003.

M. Drahus, C. Turquat, M.P. Harmer and H.M. Chan, "The Effect of Tungsten Doping on the Densification and Grain Growth of Alumina," 105th Annual Meeting of the American Ceramic Society, Nashville, TN, April 27 - 30, 2003.

## Inventions, Patent Disclosures

None

## Honors/Awards

H.M. Chan and M.P. Harmer, included in ISI's list of 'Highly Cited' researchers.

M.P.Harmer, "Engineering Ingenuity Award for Distinguished Faculty," Lehigh University, 2003.